

PATENT SPECIFICATION

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(54) C₁₄ to C₂₄ DIALKYL DIMETHYL AMMONIUM CLAY GELLING AGENTS FOR UNSATURATED POLYESTER COMPOSITIONS

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to thixotropic gelling agents for liquid unsaturated polyester compositions, namely, C₁₄ to C₂₄ dialkyl dimethyl ammonium clays, particularly montmorillonites. One aspect of the invention relates to a pregel process which is critical in the novel thickening uses of such clays. A further aspect of the invention relates to gelled compositions obtained via the pregel process, particularly to gelled polyfumarate-styrene compositions and their crosslinking to reinforced plastics, particularly those reinforced with fiberglass.

The present gelling agents are well known for use with hydrocarbon solvents but not when used in the pregel technique.

U.S. Patent 3,014,001 of E. J. Murray, assigned to Reichhold Chemicals, Inc., discloses the use of onium clays, in general, as gelling agents for unsaturated polyesters containing wax. However, the patent does not disclose C₁₄ to C₂₄ dialkyl dimethyl ammonium clays as preferred organic clay gelling agents. The patent also discloses the possibility of using a styrene pregel. It describes a pregel made with monododecyl ammonium bentonite (Bentone 18C). (The word 'Bentone' is a registered Trade Mark). However, it does not recognize criticality either in using a styrene type monomer or in employing the pregel technique.

The Murray patent emphasizes the criticality of the wax component of the tack-free compositions described. However, as shown herein, when the preferred gellants of the present invention are used in the styrene pregel method, the wax component is not necessary for obtaining non-tacky crosslinked resins.

It has now been discovered that unsaturated polyester compositions can be gelled with C₁₄ to C₂₄ dialkyl dimethyl ammonium clays employing a pregel method. In the first step, a pregel is made by mixing the quaternary clay with a minor amount by weight of a styrene type aromatic vinyl monomer, preferably styrene itself. Thereafter the pregel is mixed with preferably a major amount of the unsaturated polyester to produce a clear and stable gel having highly favourable thixotropic properties. With the pregel method, unsaturated polyester gels are readily prepared and the latter can be crosslinked to produce attractive reinforced plastics.

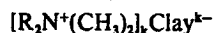
When other known quaternary ammonium clays, such as octadecyl trimethyl ammonium montmorillonite and octadecyl benzyl dimethyl ammonium clay, were used in the present pregel method, surprisingly no thixotropic compositions could be obtained. Similarly no thixotropy resulted when the C₁₄ to C₂₄ dialkyl dimethyl ammonium clay gellants were used with the typical general purpose unsaturated polyesters without employing the pregel method.

According to this invention it has been found that surprisingly stable pregels consisting of a styrene type aromatic vinyl monomer and a C₁₄ to C₂₄ dialkyl dimethyl ammonium clay are necessary for using the latter for gelling compositions containing an unsaturated polyester. The thixotropic unsaturated

polyester composition of this invention comprises an unsaturated polyester and a styrene type aromatic vinyl monomer in combination with a quaternary C₁₄ to C₂₄ dialkyl dimethyl ammonium clay in an amount sufficient to attain the desired thixotropic characteristics. The polyester is preferably present in amounts of 50 to 95% by weight of the total composition. The monomer is used preferably in amounts of 50 to 5% by weight.

C₁₄ to C₂₄ dialkyl dimethyl ammonium montmorillonites having n-alkyl groups of varying chain length have been tested as gellants with the pregel method. The dioctadecyl derivative was the most effective. In the case of the ditallow compound, an unexpected synergy of a mixture of C₁₆ and C₁₈ alkyl groups was found.

The quaternary clay gellants useful in this invention have the general formula:



wherein the two R groups which may be the same or different are C₁₄ to C₂₄ alkyl groups, preferably saturated n-alkyl groups and preferably having 16 to 18 carbon atoms; Clay is a layered or fibrous, fine grained, crystalline material which develops plasticity when mixed with limited amounts of water. Clay having high ion exchange capacities and/or aluminosilicate compositions are preferred. Such clays exhibit ion exchange capacities in the range of 50 to 150 milliequivalent exchangeable cations per 100 g clay as found by the ammonium acetate method. Three-layered type montmorillonite type clays are particularly preferred. The symbol k denotes the number of negative charges on the clay which are neutralized by positive quaternary ammonium cations.

Examples of the C₁₄ to C₂₄ alkyl groups of dialkyl dimethyl ammonium moieties of the quaternary clay gellant are ditetradecyl, dihexadecyl, diheptadecyl, dioctadecyl, dinonadecyl, dieicosyl, didocosyl, tetradecyl octadecyl, hexadecyl octadecyl, octadecyl eicosyl. Although n-alkyl groups are preferred, branched alkyl groups, particularly the slightly branched groups, specifically the primary 2-methyl-alkyl groups are also suitable.

The modified Clay^{k-} groups of the present ammonium compositions are best defined in terms of the natural and synthetic metal and ammonium aluminosilicates from which they are derived.

The natural clay starting materials of the present invention are fine grained metal aluminosilicates which develop plasticity when mixed with limited amounts of water. Similar synthetic clay derivatives are also included. For example, synthetic layered silicates, marketed as Laponites (registered Trade Mark), can be used. These Laponites have structures similar to the hectorite clay of the montmorillonite group. They are magnesium silicates of variable fluoride content.

Among the preferred clays are those having crystalline, layer type structures. For example, the three-layered type sodium montmorillonite clays can be advantageously used. Another useful clay is the chain structure type attapulgite. Two layer type clays such as kaolinites can also be used.

Further examples of clays are halloysite, smectite, illite, vermiculite, chlorite, sepiolite, palygorskite, saponite, montronite, muscovite, beidellite, biotite, micas, talcum, batavite, alleverdite, stevensite, amesite.

The quaternary ammonium clay gellants of the present invention were prepared via known ion exchange reactions, for example, between sodium montmorillonite and the corresponding C₁₄ to C₂₄ dialkyl dimethyl ammonium chlorides. The clay derivatives were prepared from equivalent amounts of the clay and quaternary salt reactants in terms of clay ion exchange capacity.

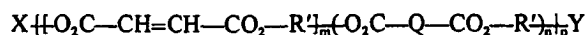
The unsaturated polyesters to be gelled according to the present invention are preferably polyesters having olefinic unsaturation of a dicarboxylic acid and a diol, particularly 10 to 75 olefin groups per 100 ester units. The unsaturation of such polyesters is preferably derived from the use of unsaturated dicarboxylic acids. The most preferred diol is propylene glycol. Such unsaturated polyesters are made by conventional esterification reactions. The molecular weight of the resulting polyester depends on the degree of esterification. This is determined by acid number and molecular weight determinations of samples. Acid numbers in the range of 35 to 45 mg KOH per g polyester resin are common. Viscosities are measured after the polyester sample is diluted with styrene. The Gardner-Holt viscosity of 60% polyester-40% styrene mixtures at 25°C is about 500 cps. These acidity and viscosity values correspond to average molecular weights of the order of 800.

Polyesters usually have molecular weights between 400 and 10,000 and have on an average 2.0 to 12 olefinic units per molecule. The latter are most preferably derived from maleates and fumarates. Maleate groups can be converted to fumarate groups via cis-trans isomerization. In the preferred unsaturated polyesters, there are usually 3 to 10 fumarate groups for every maleate group. Unsaturation can also be present in the diol components, for example, 1,4-butene-2-diol.

Besides the most common unsaturated dicarboxylic acid component, maleic anhydride, phthalic anhydride is another common constituent, leading to "saturated" dicarboxylic ester segments. The most common diol component is a C_1 to C_6 open chain alkane diol, preferably propylene glycol.

Since unsaturated polyesters are copolymers of varying composition, they are difficult to describe in terms of chemical formula. By varying the components and the polyesterification process, a large variety of structures can be made which are within the scope of the present invention.

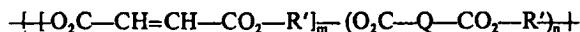
The preferred unsaturated polyesters are those of the general formula:



wherein R' is derived from the diol component and Q is derived from the "saturated" diacid component; X and Y are carboxylic acid, hydroxy or vinylic end groups; m , n and p are average numbers ranging from 0—12 defining the relative proportions of the components and the molecular weight.

R' is the hydrocarbon component of a C_2 to C_{40} substituted or unsubstituted hydrocarbon diol, the preferred substitution being ether and ester which may interrupt the hydrocarbon groups. Preferably R' is derived from a C_2 to C_{20} hydrocarbon diol. Such diols preferably consist of alkane diols and diphenols. More preferably, R' is a C_2 to C_6 alkane diol. Most preferably R' is a C_2 or C_3 diol or a mixture thereof.

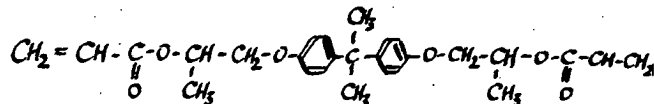
Q is the hydrocarbon component of a C_2 to C_{40} substituted or unsubstituted dicarboxylic acid or anhydride, the preferred substitutions being ether and ester groups which may interrupt the hydrocarbon groups. Preferably, Q is derived from a C_2 to C_{20} hydrocarbon dicarboxylic acid. Such dicarboxylic acids preferably consist of alkane dicarboxylic acids and aromatic dicarboxylic acids having one or more benzene rings as aromatic moieties. More preferably, Q is derived from a benzene dicarboxylic acid. The most preferred component is phthalic anhydride. The most preferred repeat unit is:



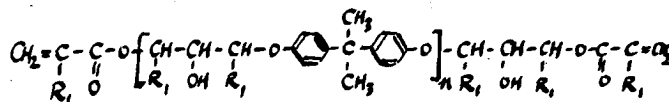
wherein R' is C_2 — C_3 alkylene, Q is phenylene and m and n are 1 to 12.

The number m ranges from 0 to 12 and as such designates the number of fumarate plus maleate units per molecule. If m is 0 there are no such units; however, in this case unsaturation is provided by X and Y being vinyl groups. The range of m and n is preferably 1 to 12.

The number n ranges from 0 to 12 and as such designates the number of saturated dicarboxylic acid ester units, usually phthalates, per molecule. If n is 0, there are no such units. However, ester functions will still be present, for example, by having propoxylated bisphenol A esterified acrylic acid, e.g.,



Similar polymers derived from epoxy resin derivatives of bisphenol A can also be used. These polymers have the general formula:

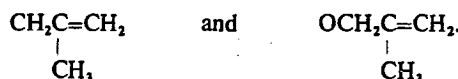


wherein R_1 is hydrogen or methyl, preferably hydrogen; n is 1 to 12. These

polymers can be regarded as polyether diol diesters with acrylic acids.

The number p also ranges from 0 to 12, and as such determines the number of repeating unsaturated plus saturated diester units. This number is preferably 0 to 6 and is clearly interrelated with the values of m and n ; p can be 0, e.g., if the unsaturation is terminal as indicated above. In any case, there is a minimum of two ester units and two unsaturated groups present per molecule. The preferred range of p is 1 to 12.

The terminating groups X and Y are preferably selected from the groups $-\text{OH}$, $-\text{ROH}$, $-\text{CO}_2\text{H}$, $-\text{QCO}_2\text{H}$, $-\text{CH}=\text{CH}_2$, $\text{O}_2\text{C}-\text{CH}=\text{CH}_2$, $\text{CH}(\text{CH}_3)=\text{CH}_2$, $\text{O}_2\text{CCH}(\text{CH}_3)\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{OCH}_2\text{CH}=\text{CH}_2$,



There is an obvious interrelationship between the hydroxyl and carboxylic acid end groups resulting from polyesterification of diol-dicarboxylic acid mixtures. In case of unsaturated terminal groups, such as acrylates, X usually equals Y .

The $\text{HO}-\text{R}-\text{OH}$ diol component is most commonly 1,2-propylene glycol. Other open chain alkane diols which can be used are ethylene glycol, 1,3-propanediol, 2,3-butylene glycol, 1,4-butane diol, 1,5-pentane diol, 2,2-dimethyl, 1,3-propane diol, decamethylene diol and a C_{20} 1,2-diol. Cyclic alkane diols are e.g., cyclohexane diol, xylylene diol, cyclohexane dimethane diol, hydrogenated bis-phenol A diol and cyclododecane diol. Aromatic diols are resorcinol, bis-phenol A and 4,4'-diphenyl diol. Ether diols are diethylene glycol, triethylene glycol, propoxylated bis-phenol A and dipropylene glycol. Examples of substituted diols are 2,3-dibromo-2-butene-1,2-diol and tetrachloroxylylene diol.

The $\text{HO}_2\text{C}-\text{Q}-\text{CO}_2\text{H}$ diacid or dianhydride component is most commonly phthalic acid or anhydride. Other common aromatic dicarboxylic acids are isophthalic acid, terephthalic acid, tetrachloroterephthalic acid, diphenic acid. Exemplary open chain alkane dicarboxylic acids are oxalic acid, succinic acid, adipic acid, sebacic acid and C_{40} dicarboxylic acids. Hydrogenated cyclic diacids can also be used such as cyclohexane dicarboxylic acid and hydrogenated dicyclopentadiene dicarboxylic acid. Substituted dicarboxylic acids are tetrachlorophthalic acid and diphenylether dicarboxylic acid.

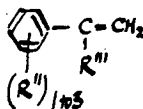
The derivation of the X and Y end groups is illustrated by the use of an excess of either one of the diacid or diol components, possibly followed by reacting with a different acid or alcohol. For example, acrylic acid or methacrylic acid can be used to provide reactive end group unsaturation. Alternatively, allyl alcohol and allyloxypropyl maleic anhydride can be used to provide allyl ether "drying functions".

The distribution of the various diester units can be statistical, e.g., in the case of one-step coesterification procedures. Alternatively, polyesters having a definite sequence of monomer units can be built step by step.

The unsaturated polyester compositions may contain 2 to 75%, preferably 5 to 50%, most preferably 20 to 45%, by weight of a styrene type monomer in admixture. Such a monomer is used in crosslinking the polyesters, preferably in the presence of a reinforcing agent. It also acts as a diluent to reduce the viscosity. As such, these monomers are essential for the reinforced plastic molding and coating uses of polyesters. These monomers are required for making the pregels of the present invention.

The styrene type monomer has a vinylic group directly attached to an aromatic nucleus such as the benzene or pyridine ring. The vinylic group can be internally substituted with methyl. However, it is preferably unsubstituted. The aromatic ring can be substituted, e.g. with C_1 to C_{12} alkyl groups and with halogen atoms such as chlorine, bromine or fluorine. However, the ring is preferably unsubstituted, e.g., phenyl or pyridyl.

The essential feature of these monomers is their activated vinylic unsaturation and aromatic character. However, the preferred compounds can be represented by the formula:

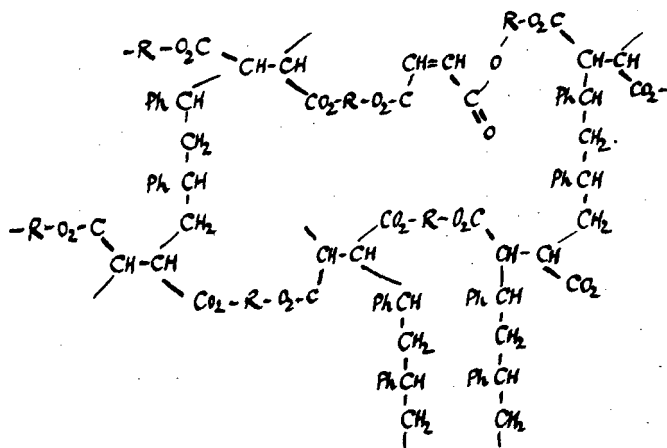


wherein R'' is methyl, chlorine, bromine or fluorine and R''' is hydrogen or methyl, preferably hydrogen. It is preferred to have not more than one R'' group, preferably chlorine or methyl. The most preferred monomer is styrene.

Exemplary other monomers are α -methyl styrene, vinyl toluene, chloro styrene, trichlorostyrene, vinyl xylene, 2-vinyl pyridine, phenyl α -methyl styrene ketone, dodecyl styrene, bromostyrene and fluorostyrene.

Other monomers, having structures outside the above definition, can be present in addition to the styrene type compounds. Such monomers can be diunsaturated or triunsaturated compounds such as divinyl benzene, diallyl phthalate, triallyl cyanurate, hexahydro triacrylo triazine or diallyl phenyl phosphonate. The use of the latter compounds results in increased crosslink densities. Another method of increasing crosslinks is the use of minor amounts of triols and polyols such as glycerol and pentaerythritol in the preparation of the resins. Other adjunct monomers can also be used. Such monomers are methyl methacrylate, methyl acrylate, vinyl acetate, acrylonitrile, N-vinyl pyrrolidone, allyl diglycol carbonate, allylidene diacetate and butyl acrylamide. Such comonomers can be selected on the basis of their copolymerization behavior and refractive index contribution.

The crosslinking of unsaturated polyesters is usually effected via free radical copolymerization with vinylic monomers. Most frequently, the fumarate unsaturation is copolymerized with styrene. The maleate unsaturation is less reactive and does not get involved. As predicted by the copolymer composition equation, the general purpose polyester which contains about 2 moles of styrene per mole of fumarate plus maleate unsaturation, appears to cure under normal conditions in such a manner that about 95% of both the styrene and fumarate unsaturation has reacted. The average crosslink consists of a bridge of two styrene molecules. There is no direct fumarate to fumarate link. Accordingly, a schematic representation of a typical crosslinked polyester network is the following.



Ph = phenyl, R = diol moiety often containing phthalate ester group.

For free radical crosslinking both chemical and radiation initiation can be employed. Preferably, chemical initiators, usually peroxides, are used. The choice of initiators depends on the desired curing temperature. For low temperature curing, peroxide-metal systems are used. Amines and mercaptans may be employed as accelerators. Other compounds such as hydrazines, quaternary ammonium salts and p-benzoquinones are used to inhibit premature crosslinking.

As shown above, such crosslinking produces stable bonds via copolymerization of the unsaturated polyester and the styrene components, usually at elevated temperatures. Therefore, the present polyester compositions can be designated as thermoset plastics.

Reinforcing fillers are preferably fibrous in character. As such, mostly glass fibers are used. Other fibrous fillers are asbestos, paper, sisal and animal fibers. Glass fibers may be surface treated for optimum reinforcing effects.

Exemplary bulk fillers are clays, such as kaolin and mica silicates, silica, chalk.

When used as coatings, unsaturated polyesters might also have present some unreactive solvents. For the production of high gloss coatings, part of the styrene may be replaced with the adipic ester of glycerol diallyl ether. The use of tetrahydrophthalic anhydride in coatings formulations leads to air drying properties. Employing glycerol α -allyl ether has a similar effect. When used in combination with such compounds, bis-isopropenyl benzene acts synergistically.

The final properties of the crosslinked resins are unexpectedly improved by the present gellants. For example, when used in the preparation of glass fiber mat reinforced polyester, the Barcol hardness of the resulting plastic is increased. This improvement is apparently inherent in the gellant content of the novel crosslinked composition.

In the process of the present invention a C_{14} to C_{24} dialkyl dimethyl ammonium clay is used to gel a styrene type monomer in the first step to form a pregel. This pregel is then mixed with an unsaturated polyester resin to form a final gel, useful in the preparation of reinforced plastics coatings and the like. The crosslinking of the gelled polyesters is the third step. It is to be understood that any of these steps can be practised independently of each other.

C_{14} to C_{24} dialkyl dimethyl ammonium clays strongly interact with styrene and similar monomers. The interaction is due to the presence of the aromatic groups in such monomers which interact with the layered organic clays. This results in an increased separation of the silicate layers of the quaternary ammonium clays which is indicated by spontaneous clay swelling and gel formation.

In the first step of the process of the present invention, pregel formation is carried out by mixing a styrene type monomer with a quaternary clay. High shear mixing is preferred. The clay may be gradually added to the monomer. In any case, pregel formation takes place usually in a few minutes, certainly within about an hour. The preferred concentration of the clay in the styrene may vary from 0.5 to 25% by weight. The clay concentration selected is dependent on the desired viscosities of the pregel and final gel. Of course, it is also dependent on the kind of quaternary clay and monomer. More preferred gellant concentrations are in the range of 2% to 12%.

Styrene pregels can be readily prepared at ambient temperatures. However, it may be preferable to use temperatures up to 100°C, especially if hot pregel is to be used without delay in the next gelling step.

In the second step of the present invention, the styrene pregel is mixed with an unsaturated polyester, the latter preferably being in a liquid state. If the polyester is a solid at room temperature, it may be heated to melt it before mixing. The viscosity of liquid polyester may be advantageously reduced by dilution with some of the styrene monomer. The styrene concentration of such polyester mixtures is then adjusted by the styrene component of the pregel. Although the gelling process does not depend on the temperature, it is preferably between 0 and 175°C.

The gelling is preferably facilitated by high shear mixing of the components. High shear mixing can be achieved by a rotary mixer having speeds preferably in the range of 20 to 13,000 rpm. Another preferred method of high shear mixing employs a roller paint mill with a preferred roller distance of 0.2—2 microns. A third method involves pebble milling. The gelling process is surprisingly rapid when pregels are used. It is substantially over within 3 hours and is usually complete within an hour.

The styrene concentration of the final gel is varied dependent on the desired balance of properties for the crosslinked final product. For example, a higher styrene concentration may be desired for higher crosslink density resulting in greater strength.

The concentration of the gelling agent should be sufficient to attain certain desired thixotropic characteristics of the resulting gel. Concentrations ranging from 0.25 to 10% by weight are preferably used.

When used in the form of the pregels of the present process, the clay layers are already separated by the styrene monomer. As a consequence, a further dispersion of the clay plates is facile and rapid. In contrast, when dry quaternary clay is added to the unsaturated polyester resin-styrene mixture, proper dispersion cannot be achieved at all and the clay settles out usually within an hour.

The gelled compositions of the present invention are truly thixotropic, i.e., they show high viscosity when not exposed to shear and this viscosity is rapidly decreased when they are subjected to increasing shear.

The quality of the clay polyester gels made via the pregel method is superior

to that of the commercial silica gels. The clay gels are clear and transparent while the silica gels are hazy and turbulent.

EXAMPLE 1.

Gelling as a Function of Chain Length of Higher Dialkyl Dimethyl Ammonium Clays.

a) Preparation of Higher Dialkyl Dimethyl Ammonium Montmorillonite Clay Gellants.

Quaternary C₁₀ to C₂₂ dialkyl dimethyl ammonium derivatives of a Wyoming montmorillonite were prepared via reactions of the corresponding ammonium chlorides with sodium montmorillonite and are summarized in Table I.

The sodium montmorillonite used was Georgia Kaolin Company's Mineral Colloid BP, a refined clay of the composition corresponding to the summary formula:



In the present work, 99 me of each of the quaternary salt reactants per 100 g dry clay was used. The quaternary ammonium chloride reactants were mostly laboratory chemicals purchased from Lachat Chemicals. Two technical quaternary ammonium chlorides, having a mixture of higher alkyl groups, were also employed. The amounts used per experiment ranged from 0.13 to 0.27 gram mole.

In general, water-isopropanol mixtures were used as reaction media. Mixtures of the same concentration were used to disperse the clay and to dissolve the quaternary salt. The concentration of the quaternary reactant solution was 10%. The concentration of the clay in the overall reaction mixture was 2%. With increasing length of the higher alkyl substituents of the quaternary salts, their water solubility decreased and consequently, the isopropanol concentrations employed increased from 0 to 50%.

In general, both the clay suspension and the quaternary solution were kept at 50°C. At that temperature, the quaternary reactant was added all at once to the clay suspension which was stirred at a high rate. This resulted in an immediate large increase of the viscosity followed in 2—3 minutes by a thinning of the mixture and the formation of the product precipitate. Stirring at 50°C was continued for 30 minutes. The mixture was then filtered with suction at the same temperature. The products were washed two times on a Buchner funnel by fresh aqueous isopropanol of the composition used in the reaction. The third wash employed water. At the 30 g starting clay level, the volume of liquid for one wash was 300 ml. Products having increasing chain length of alkyl substituents were increasingly hydrophobic and easy to filter. The washed, filtered products nevertheless still had a water content of about 90%. They were dried under 0.1 mm pressure either at ambient temperatures or at 60°C. The dry products were ball milled overnight and then passed through a 200 mesh screen. Thereafter, they were analyzed and evaluated. Their interplanar spacings of the 001 reflection by X-ray and elemental compositions are shown in Table I.

TABLE I
Preparation, Interplanar Spacing and Composition of Quaternary Higher Dialkyl Dimethyl Ammonium Montmorillonite Clays
[R₂N⁺(CH₂)_n] Cl⁻ + Clay-Na⁺ → [R₂N⁺(CH₂)_n] Clay⁻

Seq. No.	Structure of R ₂ n ⁻	i-C ₄ H ₉ OH in Water Medium, %	Salt in Reactant Medium, %	R _x Temp., °C	X-Ray Spacing d ₀₀₁ , °A	Elemental Composition of Quaternary Clay, %					
						Calcd for 99 me Salt per 100g Clay Reaction			Found		
						C	H	N	C	H	N
1	C ₁₀ H ₂₁	20	7	50	21.1-21.5	20.11	3.69	1.07	19.38	3.84	0.79
2	C ₁₂ H ₂₅	34	7	50	22.1	22.88	4.14	1.03	20.74	4.18	0.80
3	C ₁₄ H ₂₉	23	7	50	23.8	25.27	4.52	0.98	24.92	4.81	1.03
4	C ₁₆ H ₃₃	30	10	50	25.2	27.59	4.91	0.95	28.55	5.41	0.78
5	C ₁₈ H ₃₇	33	10	50	26.8	29.67	5.24	0.91	29.32	5.41	1.06
6	Tallow ^b	0	73.5	60	26.7	29.11	5.16	0.93	29.12	5.45	0.88
7	C ₃₀₋₃₂ H ₆₁₋₆₅ ^c	50	10	65	31.5	31.95	5.61	0.86	33.48	6.13	0.92

^a The same medium was used to prepare the sodium montmorillonite reactant suspension and the quaternary ammonium chloride reactant solution.

^b Di-(hydrogenated tallow)dimethyl ammonium chloride supplied by Ashland Chemical Co. in the form of a 73.5% paste in aqueous isopropanol as Adogen 442-75. The distribution of higher alkyl groups in this product is 65% C₁₈ and 5% C₁₄.

^c Di(arachidyl-behenyl)dimethyl ammonium chloride supplied by Humko Products in the form of a 75% paste as Kemamine Q-1902-C. The distribution of the higher alkyl groups in this product is 45% C₂₂, 45% C₂₀ and 10% C₁₄.

The interplanar spacing of the products, i.e. the repeat distance between the layers, was much larger than that of the starting clay, 12°A vs. 21°A or greater. The interplanar distance of the products increased with the length of the higher alkyl substituents of the quaternary nitrogen. In the case of the C₁₀ to C₁₆ derivatives the change of this distance per two carbon increase of the alkyl substituents was about 1.4°A. Overall, the definite changes in the C₁₄ to C₁₈ alkyl range were in contrast with the observations of Jordan on monoalkylammonium montmorillonites of the same range. Jordan reported no change whatsoever in this region in the "Journal of Physical and Colloid Chemistry", Volume 53, page 297 in 10

1950. This indicates an unexpected difference between the found microstructures of the present ammonium clays and of those reported previously. This microstructure is apparently differentiated by the various orientations of the higher alkyl groups between the aluminosilicate layers.

As also shown in Table I, the found elemental composition of the clays was in fair agreement with the calculated compositions assuming the attachment of all the ammonium groups to the clay. However, it is apparent that the organic contents of the di-C₁₀₋₁₂-alkyl derivatives were smaller than those of the compounds having higher dialkyl groups. This indicated a less complete ion exchange.

b) Preparation of the Styrene Pregel.

Styrene pregels were prepared usually at the 6% higher dialkyl dimethyl ammonium clay gellant level by adding the appropriate quaternary clay having less than 200 mesh particle size to polymerization grade styrene stabilized with 50 ppm t-butyl catechol. In a standard test, 3 g of gellant and 50 g styrene were placed in a 9.5 cm high, 8.5 cm diameter metal can. The contents were then stirred on a Rockwell Delta 6 Plus 6—15 in. drill press, equipped with a 5 cm wide "Cowles Blade", at 725 rpm to obtain the pregel which was then usually employed for gelling the polyester composition. Alternatively, the gellant could be added to the stirred styrene. However, the latter usually results in a less homogeneous pregel, i.e., some gellant clumps on the Cowles Blade.

At higher gellant concentrations, the pregels had a grease-like consistency since the present quaternary clays are very effective as thixotropic agents. In general, they showed a surprising stability as far as the vinyl type polymerization of styrene is concerned.

c) Preparation of the Liquid Polyfumarate Composition.

The unsaturated polyester used as a standard resin was derived via the esterification of a maleic anhydride, phthalic anhydride, propylene glycol mixture. It is commercially produced by the Reichhold Chemical Company and sold, e.g., as a 60% polyester, 40% styrene liquid mixture. During the polyesterification, most of the maleate ester groups underwent cis-trans isomerization to give fumarate ester groups.

In the present standard tests, the above solid polymaleate resin was mixed with styrene in an 80 to 20 weight ratio so as to obtain a liquid composition of high polyester content. In a typical preparation, 4,689 g of the unsaturated polyester was placed in an 11-liter four-neck flask equipped with an air-driven stirrer, water condenser, thermometer and nitrogen inlet tube. Then, 1,174 g of nitrogenated styrene containing 50 ppm t-butyl catechol and 100 ppm of p-benzoquinone was added. The resulting polyester-styrene mixture was heated to 40—45°C and allowed to stay at that temperature overnight under a mild flow of nitrogen. Then it was heated to 75—80°C over a 2-hour period and maintained at that temperature while the upper liquid phase was occasionally stirred. This resulted in an apparently homogeneous mixture which was mechanically stirred for an additional 30 minutes. The resulting pale yellow solution was allowed to cool to room temperature under a mild flow of nitrogen.

This 80% polyester-20% styrene resin was used to make gels containing 40% styrene by adding approximately one part pregel to three parts of the resin.

It was found that the viscosity of such compositions containing up to 20% styrene was too high in the absence of any clay to be useful in the present invention. The type, as well as the amount of the monomer, was critical. An attempt to use methyl methacrylate instead of styrene in the pregel method resulted in failure to obtain thixotropic compositions.

d) Preparation and Characterization of the Gelled Polyfumarate Compositions.

In a typical procedure, 52 g of the styrene pregel was added to 148 g of the liquid 80% polyester-20% styrene mixture, using stirring by drill press as described earlier. After 15 minutes' stirring, the resulting gels were closed to avoid evaporation, stored at ambient temperatures and/or at 24°C. Viscosity measurements were carried out after 15 minutes and 24 hours using a Brookfield LVT Viscometer with a number 3 spindle at 6 and 60 rpm stirring rate, generally at 24°C.

- e) Gelling Efficiency Versus Chain Length.
The viscosities of the 60% polymaleate-40% styrene resins gelled with 1.5% of the various higher di-n-C₁₂ to C₂₂-alkyl dimethyl ammonium montmorillonite clays, having 99 milliequivalent quaternary groups per 100 g clay, are shown in Table II.

TABLE II
Viscosity of Polyester-Styrene Resins (60% Solids-40% Styrene) Containing 1.5% Dialkyl C₁₀-C₂₂ Dimethyl Ammonium Montmorillonite Clays With Styrene Pregel Method

Seq. No.	Quaternary Cation on Clay	Brookfield Viscosities, cps (At Various Stirring Rates, rpm)			Viscosity Index Ratio of Viscosities at 6 and 60 rpm - After	
		After 15 Min.	After 18-24 Hrs.	After 15 Min.	15 Min.	18-24 Hrs.
1	[C ₁₀ H ₂₁) ₂ N ⁺ (CH ₃) ₂]	340	312	340	310	1.09
2	[C ₁₂ H ₂₅) ₂ N ⁺ (CH ₃) ₂]	360	324	380	346	1.11
3	[C ₁₄ H ₂₉) ₂ N ⁺ (CH ₃) ₂]	480	400	480	412	1.20
4	[C ₁₆ H ₃₃) ₂ N ⁺ (CH ₃) ₂]	720	420	720	421	1.71
5	[C ₁₈ H ₃₇) ₂ N ⁺ (CH ₃) ₂]	840	440	820	440	1.91
6	[(Tallow) ₂ N ⁺ (CH ₃) ₂]	1000	542	1000	548	1.85
7	[(C ₁₀₋₁₂ H ₁₋₁₅) ₂ N ⁺ (CH ₃) ₂]	620	404	660	423	1.53

The data of Table II show that the di-C₁₀ to C₂₂ alkyl dimethyl ammonium montmorillonites tested all increased the viscosity of the unsaturated polyester-styrene mixture, when the pregel method was used. However, only the C₁₆-C₂₂ derivatives had a significant thixotropic effect, i.e., increased the viscosity to a much greater degree at low than at high shear rates (Seq. Nos. 4-7). This thixotropic effect is expressed by the viscosity index.

The most effective gellant in the table both in terms of absolute viscosities and viscosity index is the ditallow compound (Seq. No. 6). It is interesting to observe that this compound, which on the average has less than two C₁₈ groups, is more effective than the pure di-C₁₈ compound (Seq. No. 5). The mixture of C₁₆ and C₁₈ alkyl groups in the case of the ditallow dimethyl ammonium clay has an

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unexpected synergistic effect on the gelling effectiveness. However, a similar effect, if present, is not sufficient to overcome the poorer effectiveness of the di-
C₂₂ derivative.

5 The most effective gellant, ditallow dimethyl ammonium montmorillonite, was also employed in a slightly different manner, wherein the final gelling was carried out by gradually adding 118.2 g of the solid, powdered polyester to a stirred pregel, consisting of 3.0 g of the clay and 78.8 g of styrene. Stirring of the mixture at 725 rpm was continued for 60 minutes to dissolve the ester plus an additional 15 minutes to obtain a final gel of 1.5% gellant content.

10 A comparison of the viscosities of the gels obtained using the solution and the solid techniques, as indicated by the tabulation on the following page, showed no significant difference. However, with the solid technique the gel never became transparent and showed solid haze settling after a week's standing.

TABLE IIA

Technique of Gel Preparation	Brookfield Viscosities, cps (At Various Stirring Rates, rpm)				Viscosity Index Ratio of Viscosities at 6 and 60 rpm — After	
	After 15 Min.		18–24 Hrs.			
	(6)	(60)	(6)	(60)		
Solution	1000	542	1000	548	1.85	1.82
Solid	980	600	1180	628	1.63	1.88

15 Gelling with Various Concentrations of Quaternary Ditallow Dimethyl Ammonium Derivatives of Several Commercial Montmorillonite Type Clays.

20 In the manner described in Example 1, several commercial hydrocarbon gellants were tested as gellants for unsaturated polyester-styrene mixtures via the pregel method. All the gellants had similar quaternary groups derived from dihydrogenated tallow ammonium chloride. Astratone—40 and Bentone—34 were both derived from Wyoming montmorillonites by Georgia Kaolin Company and NL Industries, Inc., respectively. Bentone—38 is also an NL product, derived from California hectorite. A similar derivative of a synthetic hectorite, Laponite, sold by Pflizer Co. as Laponite XLG, was also used for comparison. Another NL product, Bentone 27, a tallow benzyl dimethyl ammonium derivative of Wyoming montmorillonite, was also used for comparison. A fumed silica, Aerosil—200, was employed as a control. The date of the viscosity measurements, carried out at

24°C, are shown in Table III. (The word 'Aerosil' is a registered Trade Mark).

The results show that all three commercial dimethyl ditallow montmorillonite type clays and the synthetic hectorite are effective as thixotropic gellants. (Seq. Nos. 2—5). Their effectiveness is proportional to their concentration in the resin. The best gellant is Astratone—40, which at low concentrations is superior to Aerosil—200. Bentone 34 and Laponite XLG are also good gellants. All the clay gels are clear in contrast to the hazy silica gel.

It is interesting to note that Bentone—27, a montmorillonite having a different type of quaternary ammonium montmorillonite does not produce a stable gel in the polyfumarate.

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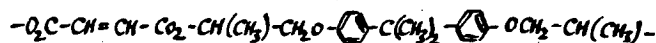
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TABLE III
Concentration Response of Commercial Gellants in Unsaturated Polyester Via Styrene Pre-Gel Method

Seq. No.	Gellant Trade Name	Gellant Conc. %	Brookfield Viscosities, cps (At Various Stirring Rates, rpm) After				Viscosity Index Ratio of Viscosities at 6 and 60 rpm After	
			15 Min.		18-24 Hrs.		15 Min.	24 Hrs.
			(6)	(60)	(6)	(60)		
1	(Control Resin)	None	280	232	280	232		
2	Astratone-40	1.0	620	396	690	432	1.57	1.57
		1.5	1400	680	1420	702	2.05	2.02
		2.0	2000	820	2460	1132	2.43	2.17
3	Bentone-34	1.0	500	392	580	394	1.28	1.32
		1.5	780	464	900	516	1.68	1.74
		2.0	1340	646	1480	692	2.07	2.14
4	Bentone-38	1.0	420	332	460	348	1.27	1.32
		1.5	700	440	680	436	1.59	1.56
		2.0	920	556	1280	824	1.65	1.55
5	Laponite XLG	1.5	720	408	720	404	1.76	1.78
6	Bentone-27	1.5	400	340	Separation		1.18	---
7	Aerosil-200	1.0	600	500	700	534	1.20	1.31
		1.5	1140	650	1280	678	1.75	1.89
		2.0	2720	980	3260	1404	2.78	2.32



and 50% styrene, was obtained from ICI America under the name Atlac 382—05A. (The word 'Atlac' is a registered Trade Mark). Such polyesters contain an average of 1 to 20 repeating units (p=1—20). In the present work, it was gelled by Astratone—40, a ditallow dimethyl ammonium montmorillonite, by several methods.

In preparation for an experiment using the pregel method of the present invention, about 46% of the styrene was removed from the polyfumarate composition by distillation in vacuo below 50° C, leaving a polyester residue having 35% styrene behind. Then 38 g of the styrene distillate was pregelled by 2.5 g Astratone in the usual manner. This pregel was then used to make the final gel by adding it to 126.4 g of the polyester residue. In this manner, a gelled, reconstituted Atlac 382—05A, containing 1.5% Astratone—40, was obtained via the pregel method.

In another experiment, 2.5 g Astratone—40 was directly added to 164.4 g of Atlac 382—05A to make the gel in the traditional manner by stirring at the 725 rpm rate. Thirdly, after a similar direct addition, the mixture was stirred at a higher shear for 15 minutes, i.e., at 3,653 rpm rather than at the usual 725 rpm.

The three gels obtained were studied for their thixotropic properties by Brookfield viscometry as usual. Similar gels were also prepared using identical amounts (i.e. 1.5%) of the commercial Aerosil—200 gellant and studied for comparison. The data are shown in Table V.

TABLE V
Thixotropic Properties of Propoxylated bis-Phenol A-Fumaric Acid Derived Polyesters
Containing 1.5% Astratone-40 Various Dispersed

Polyester: Atlac 382-05A Containing 50% Styrene; CT-117-118									
Seq. No.	Method of Dispersion	Gellant (Nil or 1.5%)	Brookfield Viscosities at 25°C, cps (At Various Stirring Rates, rpm)				Viscosity Index, i.e., Ratio of Viscosities at 6 and 60 rpm - After		
			After 15 Min.		After 18-24 Hr.		15 Min.	18-24 Hr.	
			(6)	(60)	(6)	(60)			
1	Pregel	—	500	484	520	504	1.03	1.03	1.03
2		Astratone-40	1440	1132	1460	1106	1.27	1.32	1.32
3		Aerosil-200	900	858	860	816	1.05	1.05	1.05
4	Direct	—	500	460	500	460	1.09	1.09	1.09
5		Astratone-40	580	542	520	518	1.07	1.00	1.00
6		Aerosil-200	920	940	920	896	1.02	1.03	1.03
7	High	Astratone-40	660	620	660	652	1.06	1.01	1.01
8	Shear	Aerosil	900	880	940	940	1.02	1.00	1.00

The results clearly show that using Astratone-40 in the pregel method (Seq. No. 2) resulted in the highest viscosity increase. Furthermore, even more strikingly, the only significant increase in the viscosity index was produced by Astratone-40 when used in the pregel process.

EXAMPLE 5.

Use of Ditalow Dimethyl Ammonium Montmorillonite Clay for Making an Unsaturated Polyester-Styrene Based Crosslinked Glass Fiber Reinforced Plastic.

The unsaturated polyester-styrene gel, described in Example 4, Seq. No. 3,

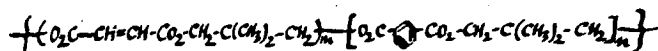
5 having 99 me ditallow dimethyl ammonium chloride treatment per 100 g clay, was used to prepare a glass reinforced plastic composition. To 100 g of each of the hand stirred gels, 0.20% of a 12% cobalt octanoate and 0.05% dimethyl aniline were added at first as peroxide decomposers. This was followed by 0.03% low molecular weight wax, in case of one of the two experiments. Finally, 1% methyl ethyl ketone peroxide crosslinking initiator was added to both compositions. Approximately 75 g of each of the resulting crosslinking compositions was then laid on three 1.5 oz. per square feet rectangular 12 x 14 cm glass mats. The resulting compositions were observed during the process of crosslinking. As characteristic crosslinking parameters gel time, tack free time and Barcol hardness were observed. The data obtained were the following:

Crosslinking Composition	Gel Time, Min. From Time of Mixing	Tack Free Time, Min., From Time of Gelling	Barcol Hardness Values, 75 Min. After Mix.
Without Wax	9.50	13.25	25-30
With Wax	9.50	21.50	1

15 The results show that the thixotropic compositions of the present invention possess the same gel time in the absence and in the presence of wax. Most surprisingly, the tack free time of the wax-free composition is shorter than that of the same composition containing wax. This means that the surface curing of the present composition is faster in the absence of wax than in its presence. This conclusion is also confirmed by data on the Barcol hardness of the two compositions 75 minutes after the mixing. These data show that, while the wax containing composition is still too soft to measure accurately, the wax free composition already has a hardness in the 25-30 range.

EXAMPLE 6.

25 Gelling of an Unsaturated Polyester Gel Coat Base with Astratone—40.
A polyfumarate derived from 2,2-dimethyl-1,3-propane diol, maleic anhydride and isophthalic anhydride, consisting of 50% of unsaturated polyester component having the repeat structural unit,



30 and about 50% styrene, containing some methylmethacrylate as a comonomer, was obtained from the Ferro Corporation, under the Gel Coat designation IE—402—I as a clear liquid. In the present work, it was gelled by Astratone—40 with the pregel method in the following manner.

35 To obtain the two basic components to be used in the pregel method, some of the styrene component of the Gel Coat was removed by distillation in vacuo at 0.15 mm using a bath of 42°C. As a result about 25% of the original composition became available as a distillate for the preparation of the pregel. The pregel preparation was carried out as usual starting with 40.8 g of the monomer distillate and 2.5 g of the Astratone—40 gellant. The resulting pregel was then added to 125.5 g of the residual component of the polyester in the usual manner to obtain a polyester gel containing 1.5% of the gellant. Using 2.5 g Aerosil—200, a silica gel was prepared in the same manner for comparison. The two gels obtained were examined for their thixotropic properties as shown in Table VI.

40 The data show that both Astratone—40 and Aerosil—200 produced compositions of moderately increased viscosity. However, the gel containing Astratone—40 was clear and stable while the Aerosil—200 gel was turbid and produced silica precipitate on standing. Although the gels produced with the low Astratone—40 concentrations were hardly thixotropic, highly thixotropic gels of increased viscosity could be readily prepared by using higher gellant concentrations.

Astratone—40 not only further increased the viscosity of the resin, but improved its thixotropic index. This was demonstrated by the preparation of a Derakane gel containing 10% Astratone—40. This was then mixed with increasing amounts of the resin to obtain reduced gellant concentrations. Determination of the viscosities of the samples obtained in the above manner showed the expected correlations as indicated by the data of Table VIII.

TABLE VII

Viscosity Characteristics of a Polyether Diacrylate Gelled With Astratone—40							
Derakane 411—50 Vinyl Ester Resin Containing 50% Styrene Plus 1.5% Gellant Via the Pregel Method							
Seq. No.	Gellant (Nil or 1.5 Wt.%)	Brookfield Viscosities at 25°C, cps (At Various Stirring Rates, rpm)				Viscosity Index, i.e., Ratio of Viscosities at 6 and 60 rpm — After	
		After 15 Min.		After 18–24 Hrs.		15 Min.	18–24 Hrs.
		(6)	(60)	(6)	(60)		
1	Nil	320	288	300	276	1.11	1.09
2	Astratone—40	480	440	480	450	1.09	1.07
3	Aerosil—200	580	560	560	546	1.04	1.03

TABLE VIII
Thixotropic Response of a Polyether Diacrylate to Varying Concentrations of Astratone-40

Derakane 411-50 Vinyl Ester Resin Containing 50% Styrene				
Seq. No.	Astratone-40 Wt. %	Brookfield Viscosities, cps (At Various Stirring Rates, rpm) Immediately After Shearing		Viscosity Index, i.e., Ratio of Viscosities at 6 and 60 rpm
		(6)	(60)	
1 ^b	Nil	320	288	1.11
2 ^a	10	31,300	6,710	4.66
3 ^a	8	17,300	4,550	3.80
4 ^b	6	5,540	1,902	2.91
5 ^b	4	1,140	852	1.34
6 ^b	3	540	506	1.07

^a Seq. Nos. 2 and 3 measured with No. 4 spindle at 28°C.

^b Seq. Nos. 1, 4, 5 and 6 measured with No. 3 spindle at 25°C.

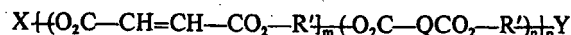
WHAT WE CLAIM IS:—

1. A thixotropic unsaturated polyester composition comprising an unsaturated polyester and a styrene type aromatic vinyl monomer in combination with a quaternary C₁₄ to C₂₄ dialkyl dimethyl ammonium clay in an amount sufficient to attain the desired thixotropic characteristics.
2. A composition according to claim 1 wherein the alkyl substituent of the quaternary dimethyl ammonium clay is C₁₆ to C₁₈ alkyl.
3. A composition according to either of claims 1 and 2 wherein the amount of unsaturated polyester ranges from 50 to 95% by weight and the amount of vinyl monomer ranges from 50 to 5% by weight of the total composition.
4. A composition according to any one of the preceding claims wherein the polyester is derived from at least a diol and a dicarboxylic acid.

5. A composition according to any one of the preceding claims wherein said polyester is derived using maleic anhydride as a principal reactant.

5 6. A composition according to any one of claims 1—4 wherein the polyester is derived from propylene glycol, maleic anhydride and phthalic anhydride and contains a styrene monomer and a minor amount of a dimethyl hydrogenated ditallow ammonium montmorillonite gelling agent. 5

7. A composition according to any one of claims 1—4 in which the polyester has the formula:



10 wherein R' is derived from the diol component; Q is derived from a saturated diacid component of the polyester; X and Y are end groups selected from carboxylic acid, hydroxy and vinyl groups; m, n and p are average numbers ranging from 0 to 12 defining the relative concentration of the components and the molecular weight; and the styrene type monomer has the formula 10



wherein R'' is methyl, chlorine, bromine or fluorine and R''' is hydrogen or methyl; and containing a minor amount by weight of a quaternary dialkyl dimethyl ammonium clay of the formula:

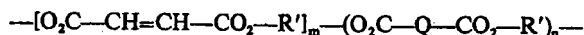


20 wherein the two R groups are each C₁₄ to C₂₄ alkyl. Clay is a layered or fibrous, fine-grained crystalline clay; k is a number denoting the number of negative charges on the clay which are neutralized by positive quaternary ammonium cations. 20

25 8. A composition according to claim 7 wherein the R' group of the polyester is derived from a C₂ to C₁₀ substituted or unsubstituted diol, Q is derived from a benzene dicarboxylic acid and X and Y are selected from carboxylic acid and hydroxy containing moieties; the R'' and R''' groups of the monomer are hydrogen; the R group of the clay is a C₁₆ to C₁₈ alkyl group and Clay is a negatively charged montmorillonite. 25

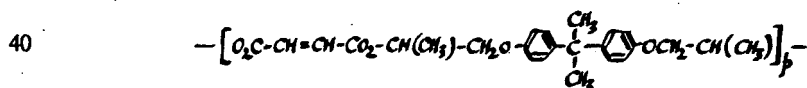
30 9. A composition according to claim 8 wherein the R' group of the polyester is derived from a C₂ to C₃ diol and Q is derived from phthalic acid. 30

10. A composition, according to any one of claims 1—4 wherein the polyester has the repeat unit,



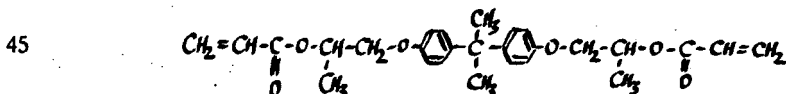
35 wherein R' is C₂—C₃ alkylene, Q is phenylene and m and n are 1 to 12, and containing styrene monomer and hydrogenated ditallow dimethyl ammonium montmorillonite. 35

11. A composition according to any one of claims 1—4 in which the polyester repeating unit has the formula:



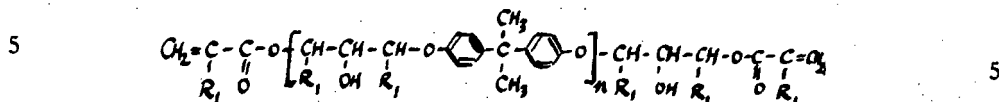
wherein p is an average number ranging from 1 to 20 and containing a styrene monomer and a hydrogenated ditallow dimethyl ammonium montmorillonite.

12. A composition according to any one of claims 1—3 in which the polyester has the formula:



and the composition contains a styrene monomer and hydrogenated ditallow dimethyl ammonium montmorillonite.

13. A composition according to any one of claims 1—3 in which the polyester has the formula



wherein R₁ is hydrogen or methyl and n is an average number ranging from 1 to 12, and the composition contains a styrene monomer and hydrogenated ditallow dimethyl ammonium montmorillonite.

14. A composition according to any one of the preceding claims wherein the amount of clay in the composition is 0.25 to 10% by weight.

15. A process for the preparation of a polyester-containing composition comprising:

- (1) mixing a styrene type aromatic vinyl monomer with a dialkyl dimethyl ammonium clay gelling agent each of said alkyl groups having 14 to 24 carbon atoms, in a minor amount by weight sufficient to provide a thixotropic pregel; and
- (2) mixing said pregel with an unsaturated polyester to provide a thixotropic gel.

16. A process according to claim 15 wherein the thixotropic gel of the second step is cross-linked.

17. A process according to claim 16 wherein the monomer of the first step is styrene, the unsaturated polyester of the second step is derived from a diol and a dicarboxylic acid and crosslinking is carried out in the presence of glass fibre as a reinforcing agent.

18. A process according to claim 17 wherein the unsaturated polyester of the second step is derived from maleic anhydride, a C₂ to C₆ alkane diol and a benzene dicarboxylic acid.

19. A process according to any one of claims 15 to 18 wherein 0.5 to 25% by weight, based on the weight of styrene type monomer, of the gelling agent are mixed in the first step.

20. A process according to claim 19 wherein the amount of gelling agent is 2 to 12% by weight.

21. A process according to any one of claims 15 to 20 wherein the gelling agent is hydrogenated ditallow dimethyl ammonium montmorillonite.

22. A polyester-containing composition whenever prepared by the process according to any one of claims 15 to 21.

23. A polyester composition according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

24. A process for preparing a polyester composition according to claim 15 substantially as hereinbefore described with reference to any one of the Examples.

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